Stochastic dynamics beyond the weak coupling limit: thermalization

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We discuss the structure and asymptotic long-time properties of coupled equations for the moments of a Brownian particle's momentum $\langle p^n(t) \rangle$ derived microscopically beyond the lowest approximation in the weak coupling parameter λ. Generalized fluctuation-dissipation relations are derived and shown to ensure convergence to thermal equilibrium to any order in λ.

I. INTRODUCTION

Many popular results of non-equilibrium statistical mechanics, such as exponential decay of correlations, hold only on a time scale much longer than the characteristic relaxation time τ_b for a thermal bath and are thus applicable only for sufficiently slow systems with relaxation time $\tau_s \gg \tau_b$. Such results may be obtained microscopically in the lowest order of the perturbation theory with the ratio $\lambda \sim \tau_b / \tau_s$ as a small parameter and, additionally, with a coarse-grained time resolution much larger than τ_b. This approximation is referred to as the weak coupling limit and can be concisely formulated as a combination of three conditions $\lambda \to 0$, $t \to \infty$, with λt finite.

There are, of course, many situations of physical interest when the weak coupling approximation does not suffice [1–3]. Van Kampen developed a highly successful theory which allows us to take into account terms of higher orders in λ, but still using as a prerequisite the time coarse graining in a form of the assumption that the system interacts with the bath via 'instantaneous' binary collisions [4]. The relaxing of this rather artificial limit leads, in general, to non-Markovian master or Langevin equations which are more difficult to handle than their Markovian counterparts. Beyond the weak coupling limit, these equations have a rather complicated structure [5, 8], and not much is known about their properties. In particular, while van Kampen's theory is consistent with equilibrium statistical mechanics [6], the relaxation to Maxwell-Boltzmann equilibrium within a more general approach, which takes into account multiple collisions and non-Markovian effects, is not entirely obvious and was questioned in several studies (see [7, 8] and references therein).

One purpose of this paper is to put the equations of stochastic dynamics into a form convenient for the evaluation of stationary solutions to any order in the weak coupling parameter λ. Most previous works in this direction seek to generalize the Fokker-Planck equation for the distribution function $f(a, t)$ for a targeted dynamical variable a. One difficulty with this approach is that beyond the lowest order in λ generalized Fokker-Planck equations involve derivatives $\partial^n f / \partial a^n$ of orders higher than two and do not guarantee positive definiteness of the solution. Also, and perhaps more importantly, within this approach it is not clear how to, in a systematic perturbative way, take into account non-Markovian effects. The same perturbation technique which justifies results in the weak coupling limit may not work well in higher orders in λ, leading to stationary distributions for the system with an equilibrium temperature different than that of the bath [8]. Neither real [9] nor numerical [10] experiments suggest such a possibility. Some other troubles with non-Markovian Fokker-Planck equations were reported in [11]. In this paper we show that some of these difficulties can be avoided if one works with microscopically derived Langevin equations for the powers a^n of a targeted variable. These equations can be readily used to derive equations for the moments $\langle a^n(t) \rangle$ which are linear and not difficult to work with even in non-Markovian form, at least as far as stationary solutions are concerned.

Although the discussion can be carried on a very general level, we choose to consider, for the sake of better visualization, the archetype example of a Brownian particle of mass M immersed in a infinitely large bath at temperature $T = 1/\beta$ and composed of molecules with mass $m \ll M$. We will employ the method by Albers et al. [12] to derive equations of motion for the moments $\langle p^n(t) \rangle$ of the Brownian particle's (scaled) momentum. It is shown that to any order in the weak coupling parameter $\lambda = (m/M)^{1/2}$ the moments relax to the equilibrium values prescribed by equilibrium statistical mechanics. Convergence to thermal equilibrium is guided by generalized fluctuation-dissipation relations, which can hardly be derived by any other method but microscopically. On the other hand, thermalization is found to be insensitive to particular relations between involved microscopic correlation functions. This leads to the optimistic conclusion that a consistent theory need not be totally microscopic.

II. EXACT EQUATIONS

Consider a system of N bath molecules of mass m interacting with each other and with a Brownian particle of mass M via short range potential U. The Hamiltonian

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of the system is $H = P^2/2M + H_0(x)$, where P is the momentum of the particle, and $H_0(x)$ is the Hamiltonian of bath molecules in the field of the particle fixed at the position x. Introducing as usual the scaled momentum of the particle $p = \lambda P$ with $\lambda = (m/M)^{1/2}$, the Liouville operator of the systems can be written as

$$L = L_0 + \lambda L_1 \tag{1}$$

where the operator L_1 acts on the particle's variables only

$$L_1 = \frac{p}{m}\frac{\partial}{\partial x} + F\frac{\partial}{\partial p}, \tag{2}$$

while L_0 governs the dynamics of the bath in the field of the fixed particle,

$$L_0 = \sum_{i=1}^{N}\left\{\frac{p_i}{m}\frac{\partial}{\partial x_i} + F_i\frac{\partial}{\partial p_i}\right\}, \tag{3}$$

and thus satisfies the relation $L_0 H_0 = 0$. In these equations x_i, p_i are coordinates and momenta of bath molecules, $F_i = -\partial U/\partial x_i$ and $F = -\partial U/\partial x$ are the forces on the ith molecules and on the particle, respectively.

We wish to decompose the exact equation

$$\frac{d}{dt}p^n(t) = e^{Lt}L\,p^n, \tag{4}$$

where $p^n = p^n(0)$, into a form convenient to derive the Langevin equation for p^n using an expansion in the small parameter λ. Using the operator identity

$$e^{\mathcal{A}t} = e^{(\mathcal{A}+\mathcal{B})t} - \int_0^t d\tau e^{\mathcal{A}(t-\tau)}\mathcal{B}e^{(\mathcal{A}+\mathcal{B})\tau}, \tag{5}$$

with $\mathcal{A} = L$, $\mathcal{B} = -\mathcal{P}L$, and $\mathcal{Q} = 1 - \mathcal{P}$ one gets

$$e^{Lt} = e^{\mathcal{Q}Lt} + \int_0^t d\tau e^{L(t-\tau)}\mathcal{P}Le^{\mathcal{Q}L\tau}. \tag{6}$$

The operator $\mathcal{P}$ is convenient to chose to be a projector operator ($\mathcal{P}^2 = \mathcal{P}$) that averages over initial values of bath variables

$$\mathcal{P}A = \langle A\rangle = \int \rho\,A\,dx_1...dx_N dp_1...dp_N \tag{7}$$

with the canonical distribution

$$\rho = \frac{1}{Z}\,e^{-\beta H_0}. \tag{8}$$

Such defined projection operator $\mathcal{P}$ and its complement $\mathcal{Q} = 1 - \mathcal{P}$ satisfy the relations

$$\mathcal{P}L_0 = 0, \qquad \mathcal{Q}L_0 = L_0. \tag{9}$$

With (6) and (9), the right-hand side of (4) can be written as

$$e^{Lt}(Lp^n) = e^{\mathcal{Q}Lt}(Lp^n) + \lambda\int_0^t d\tau e^{L(t-\tau)}\mathcal{P}L_1 e^{\mathcal{Q}L\tau}(Lp^n).$$

Then (4) takes the desirable pre-Langevin form

$$\frac{d}{dt}p^n(t) = \lambda K_n(t) + \lambda^2\int_0^t d\tau\,e^{L(t-\tau)}\mathcal{P}L_1 K_n(\tau), \tag{10}$$

where

$$K_n(t) = \lambda^{-1}e^{\mathcal{Q}Lt}Lp^n \tag{11}$$

plays the role of a "random" (rapidly fluctuating) force.

Notice that the above expression for $K_n(t)$ can be alternatively written with an additional factor $\mathcal{Q} = 1 - \mathcal{P}$:

$$K_n(t) = \lambda^{-1}e^{\mathcal{Q}Lt}\mathcal{Q}Lp^n. \tag{12}$$

This is because

$$\mathcal{P}Lp^n = \lambda\mathcal{P}L_1 p^n = \lambda n\,p^{n-1}\mathcal{P}F = \lambda n\,p^{n-1}\langle F\rangle = 0.$$

The form (12) makes it obvious that the fluctuating term $K(t)$ is zero centered

$$\langle K_n(t)\rangle = \mathcal{P}K_n(t) \sim \mathcal{P}\,\mathcal{Q} = 0. \tag{13}$$

Another useful identity involving $K_n(t)$, which can be readily proved by integrating by parts, reads

$$\left\langle\frac{\partial}{\partial x}K_n(t)\right\rangle = \mathcal{P}\frac{\partial}{\partial x}K_n(t) = -\beta\langle FK_n(t)\rangle. \tag{14}$$

Equipped with these relations, one eventually write Eq. (10) in the form

$$\begin{aligned}
\frac{d}{dt}p^n(t) &= \lambda K_n(t) \\
&+ \lambda^2\int_0^t d\tau\,e^{L(t-\tau)}\left(\frac{\partial}{\partial p} - \frac{\beta p}{m}\right)\langle F\,K_n(\tau)\rangle
\end{aligned} \tag{15}$$

with the fluctuating force

$$K_n(t) = n\,e^{\mathcal{Q}Lt}F\,p^{n-1}. \tag{16}$$

The procedure outlined above is generic and can be easily generalized to derive exact Langevin-like equation of motion for an arbitrary dynamical variable or distribution function [12].

III. LOWEST-ORDER PERTURBATION

As it is, the exact equation (15) is of little help because it contains the variables of interest p^n implicitly in the operator $e^{\mathcal{Q}Lt}$. In order to make this dependence explicit one can expand $e^{\mathcal{Q}Lt} = e^{L_0 t + \lambda\mathcal{Q}L_1 t}$ in powers of λ iteratively using the relation (5) with $\mathcal{A} = L_0$ and $\mathcal{B} = \lambda\mathcal{Q}L_1$:

$$e^{\mathcal{Q}Lt} = e^{L_0 t} + \lambda\int_0^t d\tau e^{L_0(t-\tau)}\mathcal{Q}L_1 e^{L_0\tau} \tag{17}$$

$$+\lambda^2\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\,e^{L_0(t-\tau_1)}\mathcal{Q}L_1 e^{L_0(\tau_1-\tau_2)}\mathcal{Q}L_1 e^{L_0\tau_2} + ...$$

Substitution of this into Eq.(16) for the random force $K_n(t)$ leads to the expansion

$$K_n(t) = \sum_{i=0}^{\infty} \lambda^i K_n^{(i)}(t). \qquad (18)$$

The lowest order term reads

$$K_n^{(0)}(t) = np^{n-1}F_0(t), \qquad (19)$$

where $F_0(t) = e^{L_0 t}F$ is the force exerted by the bath on the fixed particle, which can be called the pressure force. As follows from (16) and (17), the higher order terms K_i can be obtained recurrently as follows

$$K_n^{(i)}(t) = \int_0^t d\tau e^{L_0(t-\tau)} \mathcal{Q}L_1 K_n^{(i-1)}(\tau). \qquad (20)$$

Note that each term in the expansion of the random force is zero-centered, $\langle K_n^{(i)}(t)\rangle = 0$.

In the lowest order in λ the exact equation of motion (15) takes the form of the generalized Langevin equation

$$\frac{d}{dt}p^n(t) = \lambda np^{n-1}F_0(t) \qquad (21)$$

$$-\lambda^2 \frac{\beta}{m} \int_0^t d\tau\, c_0(t-\tau)\, p^n(\tau)$$

$$+\lambda^2(n-1)\int_0^t d\tau\, c_0(t-\tau)\, p^{n-2}(\tau),$$

where the memory kernel $c_0(t)$ is given by the correlation function of the pressure force,

$$c_0(t) = n\langle FF_0(t)\rangle. \qquad (22)$$

Taking the average of Eq. (21) one obtains for the moments

$$A_n(t) = \langle p^n(t)\rangle = \mathcal{P}p^n(t) \qquad (23)$$

the following equation

$$\frac{d}{dt}A_n(t) = -\lambda^2 \frac{\beta}{m} \int_0^t d\tau\, c_0(t-\tau)A_n(\tau) \qquad (24)$$

$$+\lambda^2(n-1)\int_0^t d\tau\, c_0(t-\tau)A_{n-2}(\tau).$$

In Markovian limit it takes the familiar form [13]

$$\frac{d}{dt}A_n(t) = -\lambda^2\, n\, \gamma_0 A_n(t) + \lambda^2 n(n-1)\frac{m}{\beta}\gamma_0 A_{n-2}(t) \qquad (25)$$

with the damping coefficient

$$\gamma_0 = \frac{\beta}{n\, m} \int_0^\infty dt\, c_0(t) = \frac{\beta}{m} \int_0^\infty dt\, \langle FF_0(t)\rangle. \qquad (26)$$

Of course, Eq. (25) can be derived more easily from the phenomenological Langevin equation

$$\dot{p}(t) = -\lambda^2 \gamma_0\, p(t) + \lambda F_0(t) \qquad (27)$$

under the assumption that $F_0(t)$ is Gaussian noise [13]. An important outcome of the above microscopic derivation is that it shows that the assumption of Gaussian random force is in fact unnecessary. Another advantage of the non-Markovian equation (24) is that it holds for any time, while its Markovian counterpart (25) applies only on a time scale longer than the characteristic time for the decay of the correlation function $c_0(t)$.

It is easy to show that both Markovian (25) and non-Markovian (24) equations describe relaxation of the moments to equilibrium values A_n^e prescribed by equilibrium statistical mechanics, in particular

$$A_2^e = \frac{m}{\beta}, \quad A_4^e = 3\left(\frac{m}{\beta}\right)^2, \quad A_6^e = 15\left(\frac{m}{\beta}\right)^3, \quad (28)$$

and in general for even n

$$A_n^e = (n-1)\frac{m}{\beta}A_{n-2}^e \qquad (29)$$

(equilibrium odd moments A_{2n+1}^e vanish due to symmetry). For non-Markovian equation (24), thermalization can be proved using Laplace transformation $\tilde{A}_n(s) = \int_0^\infty dt e^{-st}A_n(t)$,

$$\tilde{A}_n(s) = \frac{A_n(0)}{s + \lambda^2(\beta/m)\tilde{c}_0(s)} \qquad (30)$$

$$+ \frac{\lambda^2(n-1)\tilde{c}_0(s)}{s + \lambda^2(\beta/m)\tilde{c}_0(s)}\tilde{A}_{n-2}(s),$$

where $\tilde{A}_0(s) = 1/s$. For asymptotic long-time values

$$A_n^e = \lim_{t\to\infty} A_n(t) = \lim_{s\to 0} s\tilde{A}_n(s) \qquad (31)$$

Eq.(30) gives the thermal equilibrium result (29).

It also can be seen from from (30) that relaxation to thermal equilibrium does not occur if

$$\tilde{c}_0(s) \sim s^\delta, \quad \delta \geq 1, \quad \text{as} \quad s \to 0. \qquad (32)$$

In this case the damping coefficient γ_0 vanishes

$$\gamma_0 = \frac{\beta}{n\, m} \int_0^\infty dt\, c_0(t) = \frac{\beta}{n\, m}\tilde{c}_0(0) = 0, \qquad (33)$$

which corresponds to superdiffusion of the particle [14]. Relation (32) as a condition of non-ergodic relaxation of the second moment $A_2(t)$ was discussed in [15]. As we see, in the lowest order in λ the same condition holds for higher moments as well.

IV. HIGHER-ORDER RESULTS

As follows from (15), higher-order terms in the λ-expansion of the fluctuating force

$$K_n(t) = K_n^{(0)}(t) + \lambda K_n^{(1)}(t) + \lambda^2 K_n^{(2)}(t) + \ldots \quad (34)$$

appear in the equation for the moments A_n in the form of correlations $\langle FK_n^{(i)}(t)\rangle$. Evaluation of these correlations may be discouragingly complicated even for simplified models [16]. However, as we show in this section, a detailed evaluation of microscopic correlations is unnecessary to demonstrate convergence to thermal equilibrium to any perturbation order. All one actually needs is to find the explicit dependence of correlations $\langle FK_n^{(i)}(t)\rangle$ on the particle's momentum p, which is a much easier task.

First, recall that in the lowest order $K_0(t) = np^{n-1}F_0(t)$, so

$$\langle FK_n^{(0)}(t)\rangle = c_0(t)\,p^{n-1}, \tag{35}$$

with $c_0(t) = n\langle FF_0(t)\rangle$. Substitution of this into the exact equation (15) and taking the average leads to an equation for the moments in the form (24).

Next, it follows from the recurrence relation (20) that $K_n^{(i+1)} \sim L_1 K_n^{(i)} = [(m^{-1}\partial/\partial x)\,p + F\,\partial/\partial p]\,K_n^{(i)}$. Therefore the correlations $\langle FK_n^{(i)}(t)\rangle$ as functions of p can be obtained recurrently as follows

$$\langle FK_n^{(i+1)}(t)\rangle \sim (p + \partial/\partial p)\,\langle FK_n^{(i)}(t)\rangle. \tag{36}$$

From (35) and (36) one obtains

$$\langle FK_n^{(1)}(t)\rangle = c_{10}(t)\,p^n + c_{11}(t)\,p^{n-2}. \tag{37}$$

Explicit evaluation of the functions $c_{10}(t)$ and $c_{11}(t)$ (see Appendix) immediately reveals that for a homogeneous bath both functions vanish identically. More generally, it can be proved with the standard symmetry argument [17] that

$$\langle FK_n^{(i)}(t)\rangle = 0 \quad \text{for odd} \quad i. \tag{38}$$

Then the first non-vanishing correction to the kernel $\langle FK_n^{(0)}(t)\rangle$ is $\lambda^2\langle FK_n^{(2)}(t)\rangle$. From (37) and (36) one gets

$$\langle FK_n^{(2)}(t)\rangle = c_{20}(t)\,p^{n+1} + c_{21}(t)\,p^{n-1} + c_{22}(t)\,p^{n-3}. \tag{39}$$

Explicit expressions for the functions $c_{2i}(t)$ are not needed for our purposes, yet for the sake of completeness they are given in the Appendix. It is helpful, however, to notice that the function $c_{22}(t)$ involves the factor $(n-1)(n-2)$, which makes it vanish for $n < 3$, so that the above expression involves only positive powers of p. The same is true for higher order corrections. The next non-zero term has the form

$$\begin{aligned}\langle FK_n^{(4)}(t)\rangle &= c_{40}(t)\,p^{n+3} + c_{41}(t)\,p^{n+1} \\ &\quad + c_{42}(t)\,p^{n-1} + c_{43}(t)\,p^{n-3} + c_{44}(t)\,p^{n-5},\end{aligned} \tag{40}$$

which can be obtained by applying twice the recurrence relation (36) to the correlation $\langle FK_n^{(2)}(t)\rangle$ given by (39). The functions $c_{ij}(t)$ also depend on n. One can show that the above expression involves only positive powers of p, since $c_{43} \sim \prod_{k=1}^{3}(n-k)$ and $c_{44} \sim \prod_{k=1}^{5}(n-k)$.

With the pattern given by the above relations, the general expression can be written in the form

$$\langle FK_n^{(i)}(t)\rangle = p^{n-1}\sum_{j=0}^{i} c_{ij}(t)\,p^{i-2j}, \tag{41}$$

where $c_{ij}(t)$ vanish identically for odd i due to symmetry, and $c_{00}(t) \equiv c_0(t)$. We see that the higher the order of perturbation i, the larger the number of powers p^i to which the variable of interest p^n is coupled to.

Equipped with the above relations, one can write the equation for the moments $A_n(t) = \langle p^n(t)\rangle$ to any order in λ. As an example, let us consider the equations for the second moment A_2. In order to get the first non-zero correction to the lowest-order results discussed in the previous section, we need to expand the fluctuating force $K_2(t)$ up to order λ^2,

$$K_2(t) = K_2^{(0)}(t) + \lambda\,K_2^{(1)}(t) + \lambda^2\,K_2^{(2)}(t). \tag{42}$$

Then from (35), (38) and (39) with we get

$$\langle FK_2(t)\rangle = c_0(t)\,p + \lambda^2\left\{c_{20}(t)\,p^3 + c_{21}(t)\,p\right\}. \tag{43}$$

Substituting this into the exact equation (15) one obtains the following equation

$$\frac{d}{dt}A_2(t) = \lambda^2\left[1 - (\beta/m)\,A_2\right]\circ c_0 \tag{44}$$
$$+\lambda^4\left\{[3\,c_{20} - (\beta/m)\,c_{21}]\circ A_2 - (\beta/m)\,c_{20}\circ A_4 + c_{21}\circ 1\right\}.$$

Here and below we adopt the shorthand notation $f\circ g$ for the convolution integral $\int_0^t d\tau f(\tau)g(t-\tau)$. One observes that to the given order A_2 is coupled to A_4, which is in contrast with the lowest-order approximation where the equation for A_2 is closed.

Applying Laplace transformation one can write the long-time stationary value for A_2 as a fraction

$$\lim_{t\to\infty}A_2(t) = \lim_{s\to 0}s\tilde{A}_2(s) = \frac{N}{D} \tag{45}$$

with the denominator

$$D = \lambda^2(\beta/m)\,\tilde{c}_0(0) + \lambda^4(\beta/m)\,\tilde{c}_{21}(0) - 3\lambda^4\,\tilde{c}_{20}(0)$$

and the numerator

$$N = \lambda^2\tilde{c}_0(0) + \lambda^4\tilde{c}_{21}(0) - \lambda^4\,(\beta/m)\,\tilde{c}_{20}(0)\lim_{s\to 0}s\tilde{A}_4(s).$$

The stationary value for the fourth moment $\lim_{s\to 0}s\tilde{A}_4(s) = \lim_{t\to\infty}A_4(t)$ appears here multiplied by λ^4, and therefore the value $3(m/\beta)^2$ found in the lowest-order limit, Eq. (28), should be assigned to it. Then (45) gives for the second moment the same equilibrium value as in the lowest perturbation order, $A_2(t) \to A_2^e = m/\beta$.

Higher moments can be handled in a similar way. For instance, as follows from (35), (38) and (39), for the

fourth moment $A_4 = \langle p^4 \rangle$ the kernel $\langle FK_4(t) \rangle$ to order λ^2 takes the form

$$\langle FK_4(t) \rangle = c_0 \, p^3 + \lambda^2 \left\{ c_{20} \, p^5 + c_{21} \, p^3 + c_{22} \, p \right\}. \quad (46)$$

Substitution of this into (15) gives the equation

$$\frac{d}{dt} A_4(t) = \lambda^2 \left[3c_0 \circ A_2 - (\beta/m) \, c_0 \circ A_4 \right] \quad (47)$$

$$+ \lambda^4 \Big\{ \left[3 \, c_{21} - (\beta/m) \, c_{22} \right] \circ A_2 + \left[5 \, c_{20} - (\beta/m) \, c_{21} \right] \circ A_4$$

$$- (\beta/m) \, c_{20} \circ A_6 + c_{22} \circ 1 \Big\}.$$

Applying Laplace transform and recalling that in the lowest order $\lim_{s \to 0} s \tilde{A}_6(s) = A_6^e = 15 \, (m/\beta)^3$, one finds

$$\lim_{t \to \infty} A_4(t) = \lim_{s \to 0} s \tilde{A}_4(s) = A_4^e = 3 \, (m/\beta)^2, \quad (48)$$

which is again the equilibrium result which we already obtained in the lowest order.

No new features appear as one extends the technique to higher perturbation orders. The next non-zero correction corresponds to the expansion of the fluctuating force to order λ^4, $K_n(t) = \sum_{i=0}^{4} \lambda^i K_n^{(i)}(t)$. The correlations $\langle FK_n^{(i)}(t) \rangle$ for $i = 0, 2, 4$ are given by equations (35), (39), and (40), respectively. For example, for the second moment A_2 one obtains

$$\langle FK_2(t) \rangle = c_0 \, p + \lambda^2 \left\{ c_{20} \, p^3 + c_{21} \, p \right\} \quad (49)$$

$$+ \lambda^4 \left\{ c_{40} \, p^5 + c_{41} \, p^3 + c_{42} \, p \right\}.$$

Then substitution into (15) leads to an equation which differs from Eq.(44) by the presence of terms of order λ^6,

$$\frac{d}{dt} A_2(t) = \lambda^2 \left[1 - (\beta/m) \, A_2 \right] \circ c_0 \quad (50)$$

$$+ \lambda^4 \Big\{ \left[3 \, c_{20} - (\beta/m) \, c_{21} \right] \circ A_2 - (\beta/m) \, c_{20} \circ A_4 + c_{21} \circ 1 \Big\}$$

$$+ \lambda^6 \Big\{ \left[3 \, c_{41} - (\beta/m) \, c_{42} \right] \circ A_2 + \left[5 \, c_{40} - (\beta/m) \, c_{41} \right] \circ A_4$$

$$- (\beta/m) \, c_{40} \circ A_6 + c_{42} \circ 1 \Big\}.$$

Applying Laplace transformation and assigning equilibrium values found to lower perturbation orders for long-time limits of A_4 and A_6, one again obtains $A_2(t) \to A_2^e = m/\beta$.

V.   CONCLUSION

In the weak coupling limit, the equations for the first two moments $A_1 = \langle p \rangle$ and $A_2 = \langle p^2 \rangle$ of the Brownian particle's momentum are closed, while higher moments A_n are coupled to A_{n-2} only, see Eq. (25). To higher orders in the weak-coupling parameter λ, a larger number of moments are coupled. The higher perturbation order, the larger the number of different moments appear in the equation for A_n. In a Markovian limit the

equations coincide with those obtained by van Kampen within the instantaneous binary collision model, but contain parameters expressed in a totally microscopic way. For example, according to (44), to order λ^4 the equation for A_2 is not closed but involves coupling to A_4:

$$\frac{d}{dt} A_2(t) = -\gamma_1 A_2(t) - \gamma_2 A_4 + \gamma_3. \quad (51)$$

Dissipative coefficients γ_i are given by fluctuation-dissipation relations

$$\begin{aligned} \gamma_1 &= \lambda^2 (\beta/m) \, \alpha_0 - 3\lambda^4 \, \alpha_{20} + \lambda^4 (\beta/m) \, \alpha_{21}, \\ \gamma_2 &= \lambda^4 (\beta/m) \, \alpha_{20}, \quad (52) \\ \gamma_3 &= \lambda^2 \, \alpha_0 + \lambda^4 \, \alpha_{21}, \end{aligned}$$

Here, coefficients $\alpha_0 = \int_0^\infty c_0(t) \, dt$ and $\alpha_{2i} = \int_0^\infty c_{2i}(t) \, dt$ are system-dependent parameters, given by integrals of microscopic correlations.

Since more than one microscopic parameters α are involved in (52), it appears natural to ask whether any constraints on their relations do exist which ensure relaxation of the system to thermal equilibrium with the bath. The present paper shows that the system's thermalization is guaranteed by fluctuation-dissipation relations alone and no additional relations between microscopic parameters are required. Convergence to thermal equilibrium with the bath occurs to any order in λ, in both Markovian and non-Markovian regimes. For instance, given the asymptotic result $A_4(t) \to A_4^e = 3(m/\beta)^2$ found in the weak coupling limit, Eqs.(51) and (52) give for A_2 in the long-time limit the equilibrium value $A_2(t) \to (\gamma_3 - \gamma_2 A_4^e)/\gamma_1 = m/\beta$.

That thermalization puts no constraints on microscopic parameters α opens an attractive avenue for phenomenological modeling. One cannot use, say, Eq. (51) with arbitrary postulated values for coefficients γ_i since such an equation in general would disagree with equilibrium statistics. On the other hand, Eq.(51) supplemented with fluctuation-dissipation relations (52) for γ_i with arbitrary α is thermodynamically consistent.

Although our attention here was focused on the issue of thermalization and consistency with equilibrium statistical mechanics, most interesting applications of the developed formalism are expected, of course, for time dependent phenomena. The coupling of a larger number of moments may result in much richer dynamics compared to that in the weak coupling limit. For a Markovian limit this was illustrated in [1–3], but results from these studies may be obtained (and in fact, most of them were) within the framework of more simple van Kampen theory. For future studies, it would be interesting to identify situations where the non-Markovian form of the equations obtained in this paper would be essential and responsible for qualitatively new features. Application to Kramers' activated escape problem seems particularly promising, considering the recent demonstration that non-linear corrections to the dissipative force, which are of higher orders in λ, may be important in the underdamped regime [2].

There are several limitations of the presented study. One inevitable loophole is the tacit assumption that each term in the λ-expansion is bounded for all time. To the best of our knowledge a general proof of this is still lacking. Also, we have assumed that the relative smallness of terms is determined solely by their dependence on λ. For instance, in (52) $\gamma_2 \sim \lambda^4$ is assumed to be smaller than $\gamma_1 \sim \lambda^2$. This is not necessarily true since γ_1 involves factors which are integrated correlation functions and may vanish identically or be very small. In such situations the system may exhibit non-ergodic behavior (does not thermalize to the bath temperature) as discussed elsewhere [15]. A more exotic condition of ergodicity breaking is considered in [18].

Appendix

Exact explicit expressions for the functions $c_{ij}(t)$ in Eqs. (37) and (39) can be written respectively as

$$c_{1j}(t) = \int_0^t d\tau\, C_{1j}(t,\tau), \qquad c_{2j}(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2\, C_{2j}(t,\tau_1,\tau_2)$$

where correlation functions C_{ij} read

$$C_{10} = \frac{1}{m}\left\{ \left\langle F e^{L_0(t-\tau)}\frac{\partial F_0(\tau)}{\partial x}\right\rangle - \langle F\rangle\left\langle\frac{\partial F_0(\tau)}{\partial x}\right\rangle\right\},$$

$$C_{11} = (n-1)\left\{\langle F F_0(t-\tau)F_0(t)\rangle - \langle F\rangle\langle F F_0(\tau)\rangle\right\},$$

$$C_{20} = \frac{1}{m^2}\left\langle F e^{L_0(t-\tau_1)}\frac{\partial}{\partial x}e^{L_0(\tau_1-\tau_2)}\frac{\partial}{\partial x}F_0(\tau_2)\right\rangle,$$

$$C_{21} = \frac{n-1}{m}\left\langle F e^{L_0(t-\tau_1)}\frac{\partial}{\partial x}[F_0(\tau_1-\tau_2)F_0(\tau_1)]\right\rangle + \frac{n}{m}\left\langle F F_0(t-\tau_1)e^{L_0(t-\tau_2)}\frac{\partial}{\partial x}F_0(\tau_2)\right\rangle + \frac{\beta}{m}\langle F F_0(t-\tau_1)\rangle\langle F F_0(\tau_2)\rangle,$$

$$C_{22} = (n-1)(n-2)\left\{\langle F F_0(t-\tau_1)F_0(t-\tau_2)F_0(t)\rangle - \langle F F_0(t-\tau_1)\rangle\langle F F_0(\tau_2)\rangle\right\}.$$

Here $F = F(0) = F_0(0)$. For a homogeneous bath $C_{10} = C_{11} = 0$ by symmetry. The identity (14) was used for the derivation of the last term of C_{21}. Explicit evaluation of these and similar functions for a particular model is discussed in [16].

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